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(54) Self-cleaning coating compositions

(57) A coating composition which is capable of forming a self-cleaning coating on a surface comprises (1) a cross-linkable co-polymer of an unsaturated hydrophilic monomer and a hydrophobic co-monomer and (2) a cross-linking agent for said co-polymer, the coating composition in its hardened condition presenting a balance of hydrophilic and hydrophobic properties so as to be self-cleaning (e.g. by rain) yet sufficiently water-resistant to be durable on ourdoor exposure.

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SPECIFICATION

Self-cleaning coating compositions

Commercial growers of glasshouse crops have recognised the importance of maintaining clean glass in their greenhouses, particularly during the winter months when the amount of available sunlight is reduced. Studies have shown that a reduction in the light transmission of greenhouse glass by 10% (which commonly occurs) can result in a significant loss of yield in a cash-crop such as tomatoes. The staining of the glass which causes this loss in light transmission is believed to be due in large measure to the emissions from boilers used to heat the greenhouses and which are fired with low-grade oil having a high sulphur content. Examination of the brown staining on the glass indicates that it is an acidic material containing iron and sulphur. The stain is strongly adherent to the glass and the normal practice is to wash the glass with 1% aqueous hydrofluoric acid solution. Although this is an effective procedure, it is clearly undesirable because of the hazardous and corrosive nature of the H.F. solution.

The present invention is based on the discovery that if a transparent coating is applied to the glass which has a proper balance of hydrophilic and hydrophobic properties, the coating will resist the build-up of stains and the glass will maintain a higher light transmission level for a longer period. It is believed that this result arises from the ability of coatings to resist the adhesion of deposits which cannot be washed away by rain or water sprayed over the uncoated glass.

According to the present invention, there is provided a coating composition capable of providing a self-cleaning coating on a surface which comprises a cross-linkable co-polymer of an unsaturated hydrophilic monomer and a hydrophobic co-monomer and a cross-linking agent for said co-polymer, the coating composition in its hardened condition presenting a balance of hydrophilic and hydrophobic properties so as to be self-cleaning (e.g. by rain) yet sufficiently water-resistant to be durable on outdoor exposure. The most satisfactory hydrophilic monomers which have been tested for the purposes of the present invention are hydroxyalkyl acrylates or methacrylates among which hydroxyethyl methacrylate is preferred because of its ready commercial availability. Hydroxyalkyl methacrylates and acrylates in addition to conferring a hydrophilic character on the cured compositions of this invention have the additional advantage that they contain an hydroxyl group through which the compositions can be cured by cross-linking e.g. with a partially alkylated urea-formaldehyde resin. Satisfactory compositions have been prepared in which a hydrophilic monomer is present as a major constituent of the monomer composition but an excessive proportion of hydrophilic monomer will result in undue water sensitivity of the cured compositions and consequential breakdown of the coating when exposed to ambient conditions.

The coating compositions of this invention also include a hydrophobic co-monomer and alkyl methacrylates and acrylates have been found particularly suitable for this component. A single hydrophobic co-monomer such as methyl methacrylate may be employed although improved flexibility of the resulting co-polymers is achieved by employing a blend of methacrylates or acrylates containing a higher alkyl analogue. For example, blends of methyl methacrylate and 2-ethylhexylacrylate have been found to be very satisfactory.

Unless a two-component coating composition is employed, a cross-linking agent, such as the ureaformaldehyde resin will be incorporated in the coating composition. The cross-linking agent may be partially reacted with the co-polymer although care is required to avoid premature gelling of the co-polymer. It is usually convenient to mix the cross-linking agent with the co-polymer composition just prior to use in order to avoid premature gelling. As an alternative, the coating composition may be employed as a two-component composition, the cross-linking agent being applied to the surface to be coated separately from the co-polymer.

A preferred additional component of the coating compositions is a copolymerised unsaturated carboxylic acid such as acrylic or methacrylic acid. The presence of co-polymerised acrylic or methacrylic acid in relatively small amounts e.g. 10 to 20% has a beneficial effect on the hardness, adhesion, and water insensitivity of the resulting coatings. It is believed that it may also assist in catalysing the cross-linking reaction.

Hydroxyalkyl acrylates and methacrylates such as HEMA, contain small quantities of ethylene glycol dimethacrylate or diacrylate and higher alkyl analogues as impurities and these impurities contribute to some cross-linking of the compositions. Additional quantities of cross-linking agents of this kind can be included in the polymerisation mixture but care must be taken to avoid premature gelling of the resulting co-polymer.

The compositions of the present invention have been developed primarily for the application of colourless self-cleaning coatings to glass but their use is not restricted to such purposes and they may, for example, be used generally as self-cleaning or stain-resistant decorative coatings whether clear or pigmented. When applying coatings to glass surfaces, there is a particular problem in ensuring that a sufficient level of adhesion is obtained and it is generally advisable

when using the coatings of the present invention for coating glass to incorporate an adhesion promoter in the coating compositions or to pre treat the glass to improve the adhesion of the coatings. The preferred type of adhesion promoter is an organic silane which operates by forming a bond with the glass surface through the silane groups, the organic group of the adhesion promoter being compatible or reactive with the coating composition. Two particular types of organic silanes which have been tested satisfactorily when coating greenhouse glass with the coating compositions of this invention are organic silanes in which the organic grouping includes a methacrylate group or an aminoalkyl group.

An alternative type of adhesion promoter which can be used with the coating compositions of this invention is a perfluoroalkylphosphate type. These are surface active agents and improve adhesion of the coating compositions of this invention to glass when used at concentrations of about 1% by weight.

As indicated above, the preferred cross-linking agents are methylated urea-formaldlehyde resins, which cross-link through the hydroxyl groups of the HEMA. Concentrations in the range of from 6 to 25% of the co-polymer have been employed with preferred compositions containing about 15% by weight.

The invention includes a method of providing a self-cleaning coating on glass which comprises applying to the glass surface a coating composition comprising a cross-linkable co-polymer of a hydrophilic unsaturated monomer and a hydrophobic unsaturated co-monomer and a cross-linking agent for the co-polymer.

The co-polymer compositions of the present invention may be prepared by solution or emulsion polymerisation. A preferred procedure is to prepare the polymers by free radical polymerisation of the monomers in a solvent comprising industrial methylated spirit (IMS) or an IMS and cellosolve mixture. The coating compositions can be applied, after any necessary adjustment of the solids content of the resulting polymer solution, by spraying or brushing onto the clean surface. The following Examples are given to illustrate the preparation of compositions in accordance with the invention.

EXAMPLE 1

A co-polymer of hydroxyethyl methacrylate acrylic acid and methyl methacrylate was prepared by dissolving the monomers in the molar proportions of 3:1:4; HEMA:AA:MMA in industrial methylated spirit with azoisobutyronitrile as initiator and heating to 60–65° for 6 hours in a nitrogen atmosphere. The resulting polymer was adjusted to solids content of 22.8% by weight and mixed with the other components of the coating composition in the proportions indicated below.

	Wt. used (g)	*Solids (g)*
3: 1: 4; HEMA: AA: MMA copolymer in IMS. 22.8% solids	310	70.68
A.1100 adhesion promoter	0.71	.71
UFR 60 88% solid in propan-2-ol	10.60	9.33
Toluene-4-sulphonic acid (cross-linking catalyst)	0.71	.71
Cellosolve	174.6	
Butyl cellosolve	46.2	
	542.81	81.43

The resulting composition had a 15% solids content and 10% of the total solvent was butyl cellosolve. A.1100 adhesion promoter is available from Union Carbide and is 3-aminopropyltriethyoxysilane. UFR 60 is a methylated urea-formaldehyde resin available from Cyanamid. The resulting composition was sprayed onto greenhouse glass using a Volspray 230 spray gun at an air pressure of 40 p.s.i. Two coats were applied without waiting for the first coat to dry. In this way, a coating between 25 and 50 um thick was applied and, after drying, the coatings were tested for adhesion, water-resistance, hardness and stain-resistance. Water adhesion was assessed by two techniques, the first involving application of a fine jet of water for 24 hours to the coating and the second, immersion in water for an extended period. In the stain-resistance test, ferric chloride was employed to simulate the iron staining produced by furnace emission and a 10% ferric chloride solution was employed. It was found that this solution produced very resistant brown stains on uncoated glass but in general could be washed off coating compositions prepared in accordance with the invention. The adhesion tests involve cross-hatching of the coatings which were then tested with "Sellotape". Hardness was tested using a standard pencil hardness test. In the case of the compositions described above, the cured coatings exhibited good adhesion to the glass and remained clear or only faintly stained by ferric

chloride solution. The coating withstood the water penetration test and although the coating softened after 1½ hours immersion in water it re-hardened on removal from the water.

EXAMPLE 2

The polymer preparation described above was repeated except that the HEMA, acrylic acid and methylmethacrylate was employed in the molar proportions of 3:1:2 and the preparation was carried out in a mixture of cellosolve and industrial methylated spirits in the weight proportions of 23:27. A coating composition was prepared by mixing the following components together in the proportions indicated:–

	Wt. used (g)	*Solids (g)*
3: 1: 2; HEMA: AA: MMA copolymer in 23.27; Cellosolve: IMS 24.9% solids	280	69.72
A-174 adhesion promoter	1.56	1.56
UFR 60. 88% solids in propan-2-ol	10.46	9.20
Toluene-4-sulphonic acid	.70	.70
Cellosolve	202.50	
Butyl cellosolve	46.00	
	541.22	81.18

The resulting composition had a 15% weight solids content and 10% of the total solvent was butyl cellosolve. A-174 adhesion promoter is available from Union Carbide and is chemically 3-methacryloxypropyltrimethoxysilane. Coatings were applied to greenhouse glass for testing with similar results to those indicated above. The results in general showed that the 3:1:4; HEMA: AA: MMA based coatings exhibited better stain resistance than the 3:1:2 co-polymer coatings although the latter exhibited better adhesion. In further tests, a first coating was applied to the glass using the 3:1:2 co-polymer composition followed by a second coating of 3:1:4 co-polymer composition. Further improvements were noted when Example 2 was repeated except that in place of the co-polymer specified in that Example a co-polymer containing HEMA: AA: MMA and ethylhexylacrylate co-polymer in the proportions of a 3:1:2:1 was employed.

CLAIMS

1. A coating composition capable of providing a self-cleaning coating on a surface which comprises a cross-linkable co-polymer of an unsaturated hydrophilic monomer and a hydrophobic co-monomer and a cross-linking agent for said co-polymer, the coating composition in its hardened condition presenting a balance of hydrophilic and hydrophobic properties so as to be self-cleaning (e.g. by rain) yet sufficiently water-resistant to be durable on outdoor exposure.
2. A composition according to claim 1 wherein the hydrophilic monomer is an hydroxyalkyl acrylate or methacrylate.
3. A composition according to claim 2 wherein the cross-linking agent is a urea-formaldehyde resin which forms cross-linkages with the co-polymer through the hydroxyl groups of the hydroxyalkyl acrylate or methacrylate.
4. A composition according to anyone of the preceding claims in which the hydrophobic co-monomer is one or more alkyl acrylates or methacrylates.
5. A composition according to claim 4 in which the hydrophobic monomer comprises methyl methacrylate and a longer chain alkyl acrylate or methacrylate.
6. A composition according to any one of the preceding claims which includes an organic silane adhesion promoter.
7. A composition according to any one of claims 2 to 6 which additionally contains a copolymerised unsaturated acid.
8. A method of providing a self-cleaning coating on glass which comprises applying to the glass surface a coating composition comprising a cross-linkable co-polymer of an hydrophilic unsaturated monomer and a hydrophobic unsaturated co-monomer and a cross-linking agent for the co-polymer.
9. A method according to claim 8 in which the coating composition includes an organic silane adhesion promoter.

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